



BSR-STD-1225 (12/03)  
19 Pages

**DEPARTMENT OF LABOR & ECONOMIC GROWTH  
DIRECTOR'S OFFICE  
OCCUPATIONAL HEALTH STANDARDS**

Filed with the Secretary of State on July 25, 1989 (as amended March 26, 2001)(as amended January 15, 2002)  
This rule takes effect 7 days after filing with the Secretary of State

(By authority conferred on the director of the department of consumer and industry services by section 24 of 1974 PA 154, MCL 408.1024, and Executive Reorganization Orders Nos. 1996-1 and 1996-2, MCL 330.3101 and 445.2001)

R 325.77101 of the Michigan Administrative Code is amended as follows:  
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**PART 311. BENZENE**

**TABLE OF CONTENTS**

R 325.77101 Scope.....	1	R 325.77111 Recordkeeping.....	7
R 325.77102 Definitions.....	2	R 325.77112 Observation of monitoring.....	8
R 325.77103 Permissible exposure limits (PELs).....	2	R 325.77114 Appendices.....	8
R 325.77104 Regulated areas.....	2	R 325.77115 Availability of rules; permission to reproduce.....	8
R 325.77105 Exposure monitoring.....	2	Appendix A – Substance Safety Data Sheet.....	8
R 325.77106 Methods of compliance.....	3	Appendix B – Substance Technical Guideline.....	10
R 325.77107 Respiratory protection.....	4	Appendix C – Medical Surveillance Guidelines.....	11
R 325.77108 Protective clothing and equipment.....	5	Appendix D – Sampling and Analytical Methods for Benzene Monitoring and Measurement.....	14
R 325.77109 Medical surveillance.....	5		
R 325.77110 Communication of benzene hazards to employees.....	7		

**R 325.77101 Scope.**

**Rule 1.** (1) These rules apply to all occupational exposures to benzene, chemical abstracts service registry no. 71-43-2, except as provided in subrules (2) and (3) of this rule.

(2) These rules do not apply to any of the following:

(a) The storage, transportation, distribution, dispensing, sale, or use of gasoline, motor fuels, or other fuels that contain benzene after its final discharge from bulk wholesale storage facilities, except that operations which dispense gasoline or motor fuels for more than 4 hours per day in an indoor location are covered by these rules.

(b) Loading and unloading operations at bulk wholesale storage facilities which use vapor control systems for all loading and unloading operations. However, such operations are subject to the provisions of R 325.77107 and R 325.77109(9) and the hazard communication provisions of sections 14a to 14m of 1974 PA 154, MCL 408.1014a to 408.1014m.

(c) The storage, transportation, distribution, or sale of benzene or liquid mixtures that contain more than 0.1% benzene in intact containers or in transportation pipelines while sealed in a manner to contain benzene vapors or liquid. However, such storage, transportation, distribution, or sale is

subject to the provisions of R 325.77107 and R 325.77109(9) and the hazard communication provisions of sections 14a to 14m of 1974 PA 154, MCL 408.1014a to 408.1014m.

(d) Containers and pipelines that carry mixtures which are less than 0.1% benzene.

(e) Natural gas-processing plants that process gas which contains less than 0.1% benzene.

(f) Work operations where the only exposure to benzene is from liquid mixtures that contain 0.5% or less of benzene, by volume, or the vapors released from the liquids until September 12, 1988; work operations where the only exposure to benzene is from liquid mixtures that contain 0.3% or less of benzene, by volume, or the vapors released from the liquids from September 12, 1988, to September 12, 1989; and work operations where the only exposure to benzene is from liquid mixtures that contain 0.1% or less of benzene, by volume, or the vapors released from the liquids after September 12, 1989; except that tire-building machine operators who use solvents which contain more than 0.1% benzene are subject to the provisions of R 325.77109.

(g) Oil and gas drilling, production, and servicing operations.

(h) Coke oven batteries.

(3) Cleaning and repair operations of barges and tankers that have contained benzene are excluded from the provisions of R 325.77106, R 325.77105(1) to (4), and R 325.77105(6). Engineering and work practice controls shall be used to keep exposures below 10 ppm, unless it is proven to be not feasible.

(4) These rules replace those portions of O.H. rules 2101(5), 2101(8), and 2103 that pertain to benzene for those industries covered by subrule (1) of this rule.

## R 325.77102 Definitions.

**Rule 2.** As used in these rules:

(a) "**Act**" means 1974 PA 154, MCL 408.1001 et seq.

(b) "**Action level**" means an airborne concentration of benzene of 0.5 parts per million (ppm) calculated as an 8-hour, time-weighted average (TWA).

(c) "**Authorized person**" means any of the following:

(i) A person who is specifically authorized by the employer to enter a regulated area and whose duties require the person to enter a regulated area.

(ii) A person who enters a regulated area as a designated representative of employees for the purpose of exercising the right to observe monitoring and measuring procedures under R 325.77112.

(iii) Any other person authorized by the act or rules issued under the act.

(d) "**Benzene**" ( $C_6H_6$ ) (CAS registry no. 71-43-2) means liquefied or gaseous benzene. It includes benzene contained in liquid mixtures and the benzene vapors released by the liquids. It does not include trace amounts of unreacted benzene contained in solid materials.

(e) "**Bulk wholesale storage facility**" means a bulk terminal or bulk plant where fuel is stored before delivery to wholesale customers.

(f) "**Container**" means any barrel, bottle, can, cylinder, drum, reaction vessel, storage tank, or other receptacle, but does not include piping systems.

(g) "**Day**" means any part of a calendar day.

(h) "**Department**" means the department of consumer and industry services.

(i) "**Director**" means the director of the department or his or her designee.

(j) "**Emergency**" means any occurrence, such as, equipment failure, rupture of containers, or failure of control equipment, which may or does result in an unexpected significant release of benzene.

(k) "**Employee exposure**" means exposure to airborne benzene that would occur if an employee did not use respiratory protective equipment.

(l) "**O.H. rule**" means an occupational health rule adopted by reference in accordance with section 14 of the act. Printed copies of these rules are available for inspection and for distribution to the

public at no cost as of the time of adoption of these rules from the offices of the Michigan Department of Consumer and Industry Services, MIOSHA Standards Division, 7150 Harris Drive, Lansing, Michigan, 48909.

(m) "**Regulated area**" means any area where airborne concentrations of benzene are more than, or can reasonably be expected to be more than, the permissible exposure limits of either the 8-hour, time-weighted average exposure of 1 ppm or the short-term exposure limit of 5 ppm for 15 minutes.

(n) "**Vapor control system**" means any equipment that is used for containing the total vapors displaced during the loading of gasoline, motor fuel, or other fuel tank trucks and the displacing of these vapors through a vapor processing system or balancing the vapor with the storage tank. This equipment also includes systems containing the vapors displaced from the storage tank during the unloading of the tank truck which balance the vapors back to the tank truck.

## R 325.77103 Permissible exposure limits (PELs).

**Rule 3.** (1) An employer shall assure that an employee is not exposed to an airborne concentration of benzene of more than 1 part of benzene per million parts of air (1 ppm) as an 8-hour, time-weighted average (TWA).

(2) An employer shall assure that an employee is not exposed to an airborne concentration of benzene of more than 5 ppm averaged over any 15-minute period as a short-term exposure limit (STEL).

## R 325.77104 Regulated areas.

**Rule 4.** (1) An employer shall establish a regulated area where the airborne concentration of benzene is more than, or can reasonably be expected to be more than, the permissible exposure limits of either the 8-hour TWA exposure of 1 ppm or the STEL of 5 ppm for 15 minutes.

(2) Access to regulated areas shall be limited to authorized persons.

(3) Regulated areas shall be determined from the rest of the workplace in any manner that minimizes the number of employees exposed to benzene within the regulated area.

## R 325.77105 Exposure monitoring.

**Rule 5.** (1) Determinations of employee exposure shall be made from breathing zone air samples that are representative of each employee's average exposure to airborne benzene.

(2) Representative 8-hour TWA employee exposures shall be determined on the basis of 1 sample or samples representing the full shift exposures for each job classification in each work area.

(3) Determinations of compliance with the short-term exposure limits (STEL) shall be made from 15-minute employee breathing zone samples that are measured at operations where there is reason to

believe exposures are high, such as where tanks are opened, filled, unloaded, or gauged, where containers or process equipment are opened, and where benzene is used for cleaning or as a solvent in an uncontrolled situation. An employer may use objective data, such as measurements from brief period measuring devices, to determine where STEL monitoring is needed.

(4) Except for initial monitoring required by the provisions of subrule (5) of this rule, if an employer can document that one shift will consistently have higher exposures for an operation, then the employer shall only be required to determine representative employee exposure for that operation during the shift on which the highest exposure is expected.

(5) An employer who has a place of employment subject to these rules shall monitor each workplace and work operation to accurately determine the airborne concentrations of benzene to which employees may be exposed. Initial monitoring shall be completed within 30 days of the introduction of benzene into the workplace.

(6) If the monitoring required by subrule (5) of this rule reveals employee exposure at or above the action level, but at or below the TWA, then an employer shall repeat representative full-shift personal monitoring for each such employee at least every year. If the monitoring required by subrule (5) of this rule reveals employee exposure above the TWA, then an employer shall repeat the monitoring required by subrule (5) of this rule for each such employee at least every 6 months. An employer may alter the monitoring schedule from every 6 months to annually for an employee for whom 2 consecutive measurements, taken not less than 7 days apart, indicate that the employee exposure has decreased to the TWA or below, but is at or above the action level. Monitoring for the STEL shall be repeated as necessary to evaluate exposures of employees subject to short-term exposures.

(7) If the initial monitoring required by subrule (5) of this rule reveals employee exposure to be below the action level, then an employer may discontinue the monitoring for that employee, except as otherwise required by subrule (8) of this rule. If the periodic monitoring required by subrule (6) of this rule reveals that employee exposures, as indicated by not less than 2 consecutive measurements, taken not less than 7 days apart, are below the action level, then an employer may discontinue the monitoring for that employee, except as otherwise required by subrule (8) of this rule.

(8) An employer shall institute the exposure monitoring required by subrules (5) and (6) of this rule when there has been a change in the production, process, control equipment, personnel, or work practices which may result in new or additional exposures to benzene or when the employer has any reason to suspect a change which may result in new or additional exposures. If spills,

leaks, ruptures, or other breakdowns that may lead to employee exposure occur, then an employer shall monitor, using area or personal sampling, after the cleanup of the spill or repair of the leak, rupture, or other breakdown to ensure that exposures have returned to the level that existed before the incident.

(9) Monitoring shall be accurate, to a confidence level of 95%, to within plus or minus 25% for airborne concentrations of benzene.

(10) An employer shall, within 15 working days after the receipt of the results of any monitoring performed under these rules, notify each employee of monitoring results, in writing, either individually or by posting the results in an appropriate location that is accessible to affected employees. If the PELs are exceeded, then the written notification required by this subrule shall contain the corrective action being taken by the employer to reduce the employee exposure to or below the PELs or shall refer to a document which is available to the employee and which states the corrective actions to be taken.

### **R 325.77106 Methods of compliance.**

Rule 6. (1) An employer shall institute engineering controls and work practices to reduce and maintain employee exposure to benzene at or below the permissible exposure limits, except to the extent that the employer can establish that these controls are not feasible or where the provisions of subrule (3) of this rule or 325.77107(1) apply.

(2) Where the feasible engineering controls and work practices that can be instituted are not sufficient to reduce employee exposure to or below the PELs, an employer shall use the controls and practices to reduce employee exposure to the lowest levels that can be achieved by such use and shall supplement the controls and practices with the use of respiratory protection which complies with the requirements of R 325.77107.

(3) Where an employer can document that benzene is used in a workplace less than a total of 30 days per year, the employer shall use engineering controls, work practice controls, respiratory protection, or any combination of these controls to reduce employee exposure to benzene to or below the PELs, except that an employer shall use engineering and work practice controls, if feasible, to reduce exposure to or below 10 ppm as an 8-hour TWA.

(4) When any exposures are above the PELs, an employer shall establish and implement a written program to reduce employee exposure to or below the PELs primarily by means of engineering and work practice controls, as required by the provisions of subrule (1) of this rule. The written program shall include a schedule for development and implementation of the engineering and work practice controls. These plans shall be reviewed and revised, as appropriate, based on the most recent exposure monitoring data, to reflect the current status of the program. Upon request, written

compliance programs shall be furnished to the director, affected employees, and designated employee representatives for examination and copying.

### **R 325.77107 Respiratory protection.**

**Rule 7.** (1) For employees who use respirators required by these rules, the employer shall provide respirators that comply with the requirements of these rules. An employer shall ensure that an employee uses a respirator during all of the following:

(a) Periods necessary to install or implement feasible engineering and work-practice controls.

(b) Work operations for which the employer establishes that compliance with either the TWA or STEL through the use of engineering and work-practice controls is not feasible; for example, some maintenance and repair activities, vessel cleaning, or other operations for which engineering and work-practice controls are not feasible because exposures are intermittent and limited in duration.

(c) Work operations for which feasible engineering and work-practice controls are not yet

sufficient, or are not required under 325.77106(3), to reduce employee exposure to or below the PELs.

(d) Emergencies.

(2) An employer shall implement a respiratory protection program in accordance with 29 C.F.R. §1910.134 (b) to (d), (except for (d)(1)(iii), (d)(3)(iii)(b)(1), and (2)) and (f) to (m).

(a) For air-purifying respirators, the employer shall replace the air-purifying element at the expiration of its service life or at the beginning of each shift in which such elements are used, whichever comes first.

(b) If NIOSH approves an air-purifying element with an end-of-service-life indicator for benzene, then the element may be used until the indicator shows no further useful life.

(3) An employer shall select and provide, at no cost to the employee, the appropriate respirator from table 1 of this rule and shall ensure that the employee uses the respirator that is provided.

(4) An employer shall allow an employee who cannot use a negative-pressure respirator to use a respirator with less breathing resistance, such as a powered air-purifying respirator or supplied-air respirator.

**TABLE 1 - RESPIRATORY PROTECTION FOR BENZENE**

Airborne concentration of benzene or condition of use	Respirator type
(a) Less than or equal to 10 ppm.	Half-mask air-purifying respirator with organic vapor cartridge.
(b) Less than or equal to 50 ppm.	Full facepiece respirator with organic vapor cartridges or full facepiece gas mask with chin style canister. <sup>1</sup>
(c) Less than or equal to 100 ppm.	Full facepiece powered air-purifying respirator with organic vapor canister. <sup>1</sup>
(d) Less than or equal to 1,000 ppm.	Supplied-air respirator with full facepiece in positive-pressure mode.
(e) More than 1,000 ppm or unknown concentration.	Self-contained breathing apparatus with full facepiece positive-pressure mode or full facepiece positive-pressure supplied-air respirator with auxiliary self-contained air supply.
(f) Escape.	Any organic vapor gas mask or any self-contained breathing apparatus with full facepiece.
(g) Fire fighting.	Full facepiece self-contained breathing apparatus in positive-pressure mode.

<sup>1</sup>A canister shall have a minimum service life of 4 hours when tested at 150 ppm benzene, at a flow rate of 64 liters per minute (LPM), 25 degrees Centigrade, and 85% relative humidity for nonpowered, air-purifying respirators. The flow rate shall be 115 LPM and 170 LPM respectively for tight-fitting and loose-fitting, powered, air-purifying respirators.

**R 325.77108 Protective clothing and equipment.**

**Rule 8.** Personal protective clothing and equipment shall be worn in accordance with R 325.60001 et seq. entitled occupational health standard Part 433. Personal Protective Equipment where it is necessary to prevent eye contact and limit dermal exposure to liquid benzene. Protective clothing and equipment shall be provided by the employer at no cost to the employee and the employer shall ensure its use where appropriate. Eye and face protection shall meet the requirements of R 408.13301 et seq. entitled general industry safety standard Part 33. Personal Protective Equipment.

**R 325.77109 Medical surveillance.**

**Rule 9.** (1) An employer shall make a medical surveillance program available to all of the following persons:

(a) Employees who are or may be exposed to benzene at or above the action level 30 or more days per year.

(b) Employees who are exposed to benzene at or above the PELs 10 or more days per year.

(c) Employees who are involved in tire-building operations, known as tire-building machine operators, and who use solvents that contain more than 0.1% benzene.

(2) An employer shall ensure that all medical examinations and procedures are performed by or under the supervision of a licensed physician and that all laboratory tests are conducted by an accredited laboratory.

(3) An employer shall ensure that persons other than licensed physicians who administer the pulmonary function testing required by this rule complete a training course in spirometry sponsored by an appropriate governmental, academic, or professional institution.

(4) An employer shall ensure that all examinations and procedures are provided without cost to the employee and at a reasonable time and place.

(5) Before the time of initial assignment, an employer shall provide a medical examination for each employee covered by the provisions of this rule. The examination shall include all of the following:

(a) A detailed occupational history, including all of the following:

(i) Past work exposure to benzene or any other hematological toxins.

(ii) A family history of blood dyscrasias, including hematological neoplasms.

(iii) A history of blood dyscrasias, including genetic hemoglobin abnormalities, bleeding abnormalities, and abnormal function of formed blood elements.

(iv) A history of renal or liver dysfunction.

(v) A history of medicinal drugs routinely taken.

(vi) A history of previous exposure to ionizing radiation.

(vii) Exposure to marrow toxins outside of the current work situation.

(b) A complete physical examination.

(c) A complete blood count, including all of the following:

(i) A leukocyte count with differential.

(ii) A quantitative thrombocyte count.

(iii) Hematocrit.

(iv) Hemoglobin.

(v) Erythrocyte count and erythrocyte indices (MCV, MCH, MCHC).

The results of these tests shall be reviewed by the examining physician.

(d) Additional tests that the examining physician deems necessary due to alterations to the components of the blood or other signs which may be related to benzene exposure.

(e) For all workers who are required to wear respirators for not less than 30 days a year, the physical examination shall pay special attention to the cardiopulmonary system and shall include a pulmonary function test.

(6) An employer shall provide each employee who is subject to subrule (1) of this rule with an annual medical examination. An annual examination shall include, at a minimum, all of the following elements:

(a) A brief history regarding any new exposure to potential marrow toxins, changes in medicinal drug use, or the appearance of physical signs relating to blood disorders.

(b) A complete blood count, including all of the following:

(i) A leukocyte count with differential.

(ii) A quantitative thrombocyte count.

(iii) Hemoglobin.

(iv) Hematocrit.

(v) Erythrocyte count and erythrocyte indices (MCV, MCH, MCHC).

(c) Appropriate additional tests that the examining physician deems necessary due to alterations in the components of the blood or other signs which may be related to benzene exposure.

(7) If an employee develops signs and symptoms commonly associated with toxic exposure to benzene, then an employer shall provide the employee with an additional medical examination that shall include the elements considered appropriate by the examining physician.

(8) For persons who are required to use respirators for not less than 30 days a year, a pulmonary function test shall be performed every 3 years. A specific evaluation of the cardiopulmonary system shall be made at the time of the pulmonary function test.

(9) If an employee is exposed to benzene in an emergency situation, then, in addition to the surveillance required by these rules, the employer

shall ensure the employee has urinary phenol testing as follows:

(a) A urine sample shall be collected at the end of the employee's shift and tested within 72 hours of collection. The urine sample specific gravity shall be corrected to 1.024.

(b) If the results of the urinary phenol test is below 75 mg phenol/L of urine, then further testing is not required.

(c) If the results of the urinary phenol test is equal to or more than 75 mg phenol/L of urine, then the employee shall have an initial complete blood count to be repeated every month for 3 months, which shall include all of the following:

- (i) Erythrocyte count.
- (ii) Leukocyte count with differential.
- (iii) Thrombocyte count.

(d) If any of the conditions specified in subrule (10) of this rule exists, then the employer shall ensure that the requirements of subrule (10) are met and provide the employee with periodic examinations if directed by the physician.

(10)(a) If the results of the complete blood count required for the initial and periodic examinations indicate that any of the following abnormal conditions exist, then the employer shall ensure that the blood count is repeated within 2 weeks:

(i) The hemoglobin level or the hematocrit falls below the normal limit, that is, outside the 95% confidence interval (C.I.), as determined by the laboratory for the particular geographic area or these indices show a persistent downward trend from the individual's preexposure norms and these findings cannot be explained by other medical reasons.

(ii) The thrombocyte (platelet) count varies more than 20% below the employee's most recent values or falls outside the normal limit (95% C.I.) as determined by the laboratory.

(iii) The leukocyte count is below 4,000 per mm<sup>3</sup> or there is an abnormal differential count.

(b) If the abnormality persists, then the employer shall ensure that the examining physician shall refer an employee to a hematologist or an internal medicine physician (internist) for further evaluation, unless the physician has good reason to believe the referral is unnecessary. (See appendix C for examples of conditions where a referral may be unnecessary.)

(c) An employer shall provide the hematologist or internist with all the information required in subrule (11) of this rule and the medical record required to be maintained by R 325.77111(2).

(d) An employer shall ensure that the hematologist's or internist's evaluation includes a determination as to the need for additional tests, and an employer shall ensure that the needed tests are provided.

(11) An employer shall provide all of the following information to the examining physician:

(a) A copy of these rules and adopted appendices.

(b) A description of the affected employee's duties as they relate to the employee's exposure.

(c) The employee's actual or representative exposure level.

(d) A description of any personal protective equipment used or to be used.

(e) Information from previous employment-related medical examinations of the affected employee that is not otherwise available to the examining physician.

(12) For each examination under this rule, an employer shall obtain, and provide an employee with, a copy of the examining physician's written opinion within 15 days of the examination. The written opinion shall be limited to the following information:

(a) The occupationally pertinent results of the medical examination and tests.

(b) The physician's opinion concerning whether the employee has any detected medical conditions that would place an employee's health at greater than normal risk of material impairment from exposure to benzene.

(c) The physician's recommended limitations upon an employee's exposure to benzene or upon an employee's use of protective clothing or equipment and respirators.

(d) A statement that an employee has been informed by a physician of the results of the medical examination and any medical conditions resulting from benzene exposure that require further explanation or treatment.

The written opinion obtained by an employer shall not reveal specific records, findings, and diagnoses that have no bearing on the employee's ability to work in a benzene-exposed workplace.

(13) If a physician makes a referral to a hematologist or internist under subrule (10) of this rule, then an employee shall be removed from areas where exposures may exceed the action level until the physician makes a determination under subrule (14) of this rule.

(14) Following the examination and evaluation by a hematologist or internist, a decision to remove an employee from areas where benzene exposure is above the action level or to allow the employee to return to areas where benzene exposure is above the action level shall be made by the physician in consultation with the hematologist or internist. The physician shall communicate the decision, in writing, to the employer and employee. In the case of removal, the physician shall state the required probable duration of removal from occupational exposure to benzene above the action level and the requirements for future medical examinations to review the decision.

(15) If an employee is removed under subrule (14) of this rule, then an employer shall provide a follow-up examination. The physician, in consultation with the hematologist or internist, shall make a decision, within 6 months of the date an

employee was removed, as to whether the employee shall be returned to his or her usual job or whether the employee should be removed permanently.

(16) If an employee is temporarily removed from benzene exposure under subrule (13) or (14) of this rule, then an employer shall transfer the employee to a comparable job for which the employee is qualified or which the employee can be trained for in a short period and where benzene exposures are as low as possible, but not higher than the action level. An employer shall maintain the employee's current wage rate, seniority, and other benefits. If no such job is available, then an employer shall provide medical removal protection benefits until a job becomes available or for 6 months, whichever comes first.

(17) If an employee is removed permanently from benzene exposure based on a physician's recommendation under subrule (15) of this rule, then an employee shall be given the opportunity to transfer to another position which is available or later becomes available for which the employee is qualified or which the employee can be trained for in a short period and where benzene exposures are as low as possible, but not higher than the action level. An employer shall ensure that the employee does not suffer a reduction in current wage rate, seniority, or other benefits as a result of the transfer.

(18) An employer shall provide to an employee 6 months of medical removal protection benefits immediately following each occasion that an employee is removed from exposure to benzene because of hematological findings under subrule (13) or (14) of this rule, unless the employee has been transferred to a comparable job where benzene exposures are below the action level.

(19) For the purposes of this rule, the requirement that an employer provide medical removal protection benefits means that the employer shall maintain the current wage rate, seniority, and other benefits of an employee as though the employee had not been removed.

(20) An employer's obligation to provide medical removal protection benefits to a removed employee shall be reduced to the extent that the employee receives compensation for earnings lost during the period of removal either from a publicly or employer-funded compensation program or from employment with another employer made possible by virtue of the employee's removal.

### **R 325.77110 Communication of benzene hazards to employees.**

**Rule 10.** (1) An employer shall post signs at entrances to regulated areas. The signs shall bear the following legend:

**DANGER  
BENZENE  
CANCER HAZARD  
FLAMMABLE - NO SMOKING  
AUTHORIZED PERSONNEL ONLY  
RESPIRATOR REQUIRED**

(2) An employer shall ensure that labels or other appropriate forms of warning are provided for containers of benzene within the workplace. The labels shall comply with the hazard communication provisions of sections 14a to 14m of 1974 PA 154, MCL 408.1014a to 408.1014m and, in addition, shall include the following legend:

**DANGER  
CONTAINS BENZENE  
CANCER HAZARD**

(3) An employer shall obtain or develop, and provide its employees access to, a material safety data sheet (MSDS) which addresses benzene and complies with the hazard communication provisions referenced in subrule (2) of this rule. An employer who is a manufacturer or importer shall comply with the provisions of this subrule and with the hazard communication provisions referenced in subrule (2) of this rule, that the employer deliver to downstream employers an MSDS that addresses benzene.

(4) An employer shall provide employees with information and training at the time of their initial assignment to a work area where benzene is present. If exposures are above the action level, then employees shall be provided with information and training at least annually thereafter. The training program shall comply with the hazard communication provisions referenced in subrule (2) of this rule and shall include specific information on benzene for each category of information included in sections 14a to 14m of 1974 PA 154, MCL 408.1014a to 408.1014m. In addition to the information required, pursuant to the hazard communication provisions referenced in subrule (2) of this rule, the employer shall do both of the following:

(a) Provide employees with an explanation of the contents of this rule, including appendices A and B, which are adopted by reference in R 325.77114, and indicate to employees where copies of these rules are available.

(b) Describe the medical surveillance program required under R 325.77109 and explain the information contained in appendix C.

### **R 325.77111 Recordkeeping.**

**Rule 11.** (1) An employer shall establish and maintain an accurate record of all measurements required by R 325.77105 in accordance with the provisions of the occupational health standard, Employee Medical Records and Trade Secrets, being R 325.3451 et seq. The record shall include all of the following information:

(a) The dates, number, duration, and results of each of the samples taken, including a description of the procedure used to determine representative employee exposures.

(b) A description of the sampling and analytical methods used.

(c) A description of the type of respiratory protective devices worn, if any.

(d) The name, social security number, job classification, and exposure levels of the employee monitored and all other employees whose exposures the measurement is intended to represent.

An employer shall maintain this record for not less than 30 years and in accordance with R 325.3451 to R 325.3476.

(2) An employer shall establish and maintain an accurate record for each employee who is subject to medical surveillance required by the provisions of R 325.77109. The record shall be maintained in accordance with R 325.3451 to R 325.3476. The record shall include all of the following information:

(a) The name and social security number of the employee.

(b) The employer's copy of the physician's written opinion on the initial, annual, and special examinations, including results of medical examinations and all tests, opinions, and recommendations.

(c) Any employee medical complaints related to exposure to benzene.

(d) A copy of the information provided to the physician as required by R 325.77109(11)(b) to (e).

(e) A copy of the employee's medical and work history related to exposure to benzene or any other hematologic toxins.

An employer shall maintain the record for not less than the duration of employment plus 30 years. The record shall be maintained in accordance with R 325.3451 to R 325.3476.

(3) An employer shall ensure that all records required to be maintained by this rule shall be made available, upon request, to the director for examination and copying. Employee exposure monitoring records required by this rule shall be provided, upon request, for examination and copying to employees, employee representatives, and the director in accordance with R 325.3451 to R 325.3476. Employee medical records required by this rule shall be provided, upon request, for examination and copying to the subject employee, to anyone having the specific written consent of the subject employee, and to the director in accordance with R 325.3451 to R 325.3476.

(4) An employer shall comply with the requirements involving the transfer of records set forth in R 325.3475. If an employer ceases to do business and there is no successor employer to receive and retain the records for the prescribed period, then the employer shall notify the director not less than 3 months before disposal and transmit

them to the director if required by the director within that period.

#### **R 325.77112 Observation of monitoring.**

**Rule 12.** (1) An employer shall provide affected employees or their designated representatives an opportunity to observe the measuring of monitoring of employee exposure to benzene conducted pursuant to the provisions of R 325.77105.

(2) When observation of the measuring or monitoring of employee exposure to benzene requires entry into areas where the use of protective clothing and equipment or respirators is required, an employer shall provide the observer with personal protective clothing and equipment or respirators required to be worn by employees working in the area, assure the use of such clothing and equipment or respirators, and require the observer to comply with all other applicable safety and health procedures.

#### **R 325.77113 Rescinded (04/03/01).**

#### **R 325.77114 Appendices.**

**Rule 14.** Appendices A, B, C, and D are informational and are not intended to create any additional obligations not otherwise imposed or to detract from any existing obligations.

#### **R 325.77115 Availability of rules; permission to reproduce.**

**Rule 15.** (1) Printed copies of these rules are available for inspection and for distribution to the public at no cost at the offices of the Michigan Department of Consumer and Industry Services, MIOSHA Standards Division, 7150 Harris Drive, Lansing, Michigan, 48909.

(2) Permission to reproduce any of these documents in full is granted by the director.

### **APPENDICES TO MIOSHA STANDARD FOR BENZENE (R 325.77101-R 325.77115)**

#### **APPENDIX A SUBSTANCE SAFETY DATA SHEET**

##### **I. Substance Identification**

A. Substance: Benzene.

B. Permissible Exposure: Except as to the use of gasoline, motor fuels and other fuels subsequent to discharge from bulk terminals and other exemptions specified in 1910.1028(a)(2):

1. Airborne: The maximum time-weighted average (TWA) exposure limit is 1 part of benzene vapor per million parts of air (1 ppm) for an 8-hour workday



and the maximum short-term exposure limit (STEL) is 5 ppm for any 15-minute period.

2. Dermal: Eye contact shall be prevented and skin contact with liquid benzene shall be limited.

C. Appearance and odor: Benzene is a clear, colorless liquid with a pleasant, sweet odor. The odor of benzene does not provide adequate warning of its hazard.

## II. Health Hazard Data

A. Ways in which benzene affects your health. Benzene can affect your health if you inhale it, or if it comes in contact with your skin or eyes. Benzene is also harmful if you happen to swallow it.

B. Effects of overexposure. 1. Short-term (acute) overexposure: If you are overexposed to high concentrations of benzene, well above the levels where its odor is first recognizable, you may feel breathless, irritable, euphoric, or giddy; you may experience irritation in eyes, nose, and respiratory tract. You may develop a headache, feel dizzy, nauseated, or intoxicated. Severe exposures may lead to convulsions and loss of consciousness.

2. Long-term (chronic) exposure. Repeated or prolonged exposure to benzene, even at relatively low concentrations, may result in various blood disorders, ranging from anemia to leukemia, an irreversible, fatal disease. Many blood disorders associated with benzene exposure may occur without symptoms.

## III. Protective Clothing and Equipment

A. Respirators. Respirators are required for those operations in which engineering controls or work practice controls are not feasible to reduce exposure to the permissible level. However, where employers can document that benzene is present in the workplace less than 30 days a year, respirators may be used in lieu of engineering controls. If respirators are worn, they must have joint Mine Safety and Health Administration and the National Institute for Occupational Safety and Health (NIOSH) seal of approval, and cartridge or canisters must be replaced before the end of their service life, or the end of the shift, whichever occurs first. If you experience difficulty breathing while wearing a respirator, you may request a positive pressure respirator from your employer. You must be thoroughly trained to use the assigned respirator, and the training will be provided by your employer.

B. Protective Clothing. You must wear appropriate protective clothing (such as boots, gloves, sleeves, aprons, etc.) over any parts of your body that could be exposed to liquid benzene.

C. Eye and Face Protection. You must wear splash-proof safety goggles if it is possible that benzene may get into your eyes. In addition, you must wear a face shield if your face could be splashed with benzene liquid.

## IV. Emergency and First Aid Procedures

A. Eye and face exposure. If benzene is splashed in your eyes, wash it out immediately with large amounts of water. If irritation persists or vision appears to be affected see a doctor as soon as possible.

B. Skin exposure. If benzene is spilled on your clothing or skin, remove the contaminated clothing and wash the exposed skin with large amounts of water and soap immediately. Wash contaminated clothing before you wear it again.

C. Breathing. If you or any other person breathes in large amounts of benzene, get the exposed person to fresh air at once. Apply artificial respiration if breathing has stopped. Call for medical assistance or a doctor as soon as possible. Never enter any vessel or confined space where the benzene concentration might be high without proper safety equipment and at least one other person present who will stay outside. A life line should be used.

D. Swallowing. If benzene has been swallowed and the patient is conscious, do not induce vomiting. Call for medical assistance or a doctor immediately.

## V. Medical Requirements

If you are exposed to benzene at a concentration at or above 0.5 ppm as an 8-hour time-weighted average, or have been exposed at or above 10 ppm in the past while employed by your current employer, your employer is required to provide a medical examination and history and laboratory tests within 60 days of the effective date of this standard and annually thereafter. These tests shall be provided without cost to you. In addition, if you are accidentally exposed to benzene (either by ingestion, inhalation, or skin/eye contact) under emergency conditions known or suspected to constitute toxic exposure to benzene, your employer is required to make special laboratory tests available to you.

## VI. Observation of Monitoring

Your employer is required to perform measurements that are representative of your exposure to benzene and you or your designated representative are entitled to observe the monitoring procedure. You are entitled to observe the steps taken in the measurement procedure, and to record the results obtained. When the monitoring procedure is taking

place in an area where respirators or personal protective clothing and equipment are required to be worn, you or your representative must also be provided with, and must wear the protective clothing and equipment.

## VII. Access to Records

You or your representative are entitled to see the records of measurements of your exposure to benzene upon written request to your employer. Your medical examination records can be furnished to yourself, your physician or designated representative upon request by you to your employer.

## VIII. Precautions for Safe Use, Handling and Storage

Benzene liquid is highly flammable. It should be stored in tightly closed containers in a cool, well ventilated area. Benzene vapor may form explosive mixtures in air. All sources of ignition must be controlled. Use nonsparking tools when opening or closing benzene containers. Fire extinguishers, where provided, must be readily available. Know where they are located and how to operate them. Smoking is prohibited in areas where benzene is used or stored. Ask your supervisor where benzene is used in your area and for additional plant safety rules.

## APPENDIX B SUBSTANCE TECHNICAL GUIDELINES

### I. Physical and Chemical Data

#### A. Substance identification.

1. Synonyms: Benzol, benzole, coal naphtha, cyclohexatriene, phene, phenyl hydride, pyrobenzol. (Benzin, petroleum benzin and Benzine do not contain benzene).

2. Formula: C(6)H(6) (CAS Registry Number: 71-43-2)

#### B. Physical data.

1. Boiling Point (760 mm Hg); 80.1 deg. C (176 deg. F)

2. Specific Gravity (water = 1): 0.879

3. Vapor Density (air = 1): 2.7

4. Melting Point: 5.5 deg. C (42 deg. F)

5. Vapor Pressure at 20 deg. C (68 deg. F): 75 mm Hg

6. Solubility in Water: .06%

7. Evaporation Rate (ether = 1): 2.8

8. Appearance and Odor: Clear, colorless liquid with a distinctive sweet odor.

### II. Fire, Explosion, and Reactivity Hazard Data

#### A. Fire.

1. Flash Point (closed cup): - 11 deg. C (12 deg. F)

2. Autoignition Temperature: 580 deg. C (1076 deg. F)

3. Flammable limits in Air. % by Volume: Lower: 1.3%, Upper: 7.5%

4. Extinguishing Media: Carbon dioxide, dry chemical, or foam.

5. Special Fire-Fighting procedures: Do not use solid stream of water, since stream will scatter and spread fire. Fine water spray can be used to keep fire-exposed containers cool.

6. Unusual fire and explosion hazards: Benzene is a flammable liquid. Its vapors can form explosive mixtures. All ignition sources must be controlled when benzene is used, handled, or stored. Where liquid or vapor may be released, such areas shall be considered as hazardous locations. Benzene vapors are heavier than air; thus the vapors may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which benzene is handled.

7. Benzene is classified as a 1 B flammable liquid for the purpose of conforming to the requirements of 29 CFR 1910.106. A concentration exceeding 3,250 ppm is considered a potential fire explosion hazard. Locations where benzene may be present in quantities sufficient to produce explosive or ignitable mixtures are considered Class I Group D for the purposes of conforming to the requirements of 29 CFR 1910.309.

#### B. Reactivity.

1. Conditions contributing to instability: Heat.

2. Incompatibility: Heat and oxidizing materials.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide).

### III. Spill and Leak Procedures

A. Steps to be taken if the material is released or spilled. As much benzene as possible should be absorbed with suitable materials, such as dry sand

or earth. That remaining must be flushed with large amounts of water. Do not flush benzene into a confined space, such as a sewer, because of explosion danger. Remove all ignition sources. Ventilate enclosed places.

B. Waste disposal method. Disposal methods must conform to other jurisdictional regulations. If allowed, benzene may be disposed of: (a) By absorbing it in dry sand or earth and disposing in a sanitary landfill; (b) if small quantities, by removing it to a safe location from buildings or other combustible sources, pouring it in dry sand or earth and cautiously igniting it; and (c) if large quantities, by atomizing it in a suitable combustion chamber.

#### **IV. Miscellaneous Precautions**

A. High exposure to benzene can occur when transferring the liquid from one container to another. Such operations should be well ventilated and good work practices must be established to avoid spills.

B. Use non-sparking tools to open benzene containers which are effectively grounded and bonded prior to opening and pouring.

C. Employers must advise employees of all plant areas and operations where exposure to benzene could occur. Common operations in which high exposures to benzene may be encountered are: the primary production and utilization of benzene, and transfer of benzene.

### **APPENDIX C MEDICAL SURVEILLANCE GUIDELINES**

#### **I. Route of Entry**

Inhalation; skin absorption.

#### **II. Toxicology**

Benzene is primarily an inhalation hazard. Systemic absorption may cause depression of the hematopoietic system, pancytopenia, aplastic anemia, and leukemia. Inhalation of high concentrations can affect central nervous system function. Aspiration of small amounts of liquid benzene immediately causes pulmonary edema and hemorrhage of pulmonary tissue. There is some absorption through the skin. Absorption may be more rapid in the case of abraded skin, and benzene may be more readily absorbed if it is present in a mixture or as a contaminant in solvents which are readily absorbed. The defatting action of benzene may produce primary irritation due to repeated or prolonged contact with the skin. High concentration are irritating to the eyes and the mucous membranes of the nose, and respiratory tract.

#### **III. Signs and Symptoms**

Direct skin contact with benzene may cause erythema. Repeated or prolonged contact may result in drying, scaling dermatitis, or development of secondary skin infections. In addition, there is benzene absorption through the skin. Local effects of benzene vapor or liquid on the eye are slight. Only at very high concentrations is there any smarting sensation in the eye. Inhalation of high concentrations of benzene may have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation, and/or giddiness, followed by a period of depression, drowsiness, or fatigue. A sensation of tightness in the chest accompanied by breathlessness may occur and ultimately the victim may lose consciousness. Tremors, convulsions and death may follow from respiratory paralysis or circulatory collapse in a few minutes to several hours following severe exposures.

The detrimental effect on the blood-forming system of prolonged exposure to small quantities of benzene vapor is of extreme importance. The hematopoietic system is the chief target for benzene's toxic effects which are manifested by alterations in the levels of formed elements in the peripheral blood. These effects have occurred at concentrations of benzene which may not cause irritation of mucous membranes, or any unpleasant sensory effects. Early signs and symptoms of benzene morbidity are varied, often not readily noticed and non-specific. Subjective complaints of headache, dizziness, and loss of appetite may precede or follow clinical signs. Rapid pulse and low blood pressure, in addition to a physical appearance of anemia, may accompany a subjective complaint of shortness of breath and excessive tiredness. Bleeding from the nose, gums, or mucous membranes, and the development of purpuric spots (small bruises) may occur as the condition progresses. Clinical evidence of leukopenia, anemia, and thrombocytopenia, singly or in combination, has been frequently reported among the first signs.

Bone marrow may appear normal, aplastic, or hyperplastic, and may not, in all situations, correlate with peripheral blood forming tissues. Because of variations in the susceptibility to benzene morbidity, there is no "typical" blood picture. The onset of effects of prolonged benzene exposure may be delayed for many months or years after the actual exposure has ceased and identification or correlation with benzene exposure must be sought out in the occupational history.

#### **IV. Treatment of Acute Toxic Effects**

Remove from exposure immediately. Make sure you are adequately protected and do not risk being

overcome by fumes. Give oxygen or artificial resuscitation if indicated. Flush eyes, wash skin if contaminated and remove all contaminated clothing. Symptoms of intoxication may persist following severe exposures. Recovery from mild exposures is usually rapid and complete.

## V. Surveillance and Preventive Considerations

### A. General

The principal effects of benzene exposure which form the basis for this regulation are pathological changes in the hematopoietic system, reflected by changes in the peripheral blood and manifesting clinically as pancytopenia, aplastic anemia, and leukemia. Consequently, the medical surveillance program is designed to observe, on a regular basis, blood indices for early signs of these effects, and although early signs of leukemia are not usually available, emerging diagnostic technology and innovative regimes make consistent surveillance for leukemia, as well as other hematopoietic effects, essential.

Initial examinations are to be provided within 60 days of the effective date of this standard, or at the time of initial assignment, and periodic examinations annually thereafter. There are special provisions for medical tests in the event of hematologic abnormalities or for emergency situations.

The blood values which require referral to a hematologist or internist are noted in the standard in paragraph (i)(5). The standard specifies that blood abnormalities that persist must be referred "unless the physician has good reason to believe such referral is unnecessary" (paragraph (i)(5)). Examples of conditions that could make a referral unnecessary despite abnormal blood limits are iron or folate deficiency, menorrhagia, or blood loss due to some unrelated medical abnormality.

Symptoms and signs of benzene toxicity can be non-specific. Only a detailed history and appropriate investigative procedures will enable a physician to rule out or confirm conditions that place the employee at increased risk. To assist the examining physician with regard to which laboratory tests are necessary and when to refer an employee to the specialist, OSHA has established the following guidelines.

### B. Hematology Guidelines

A minimum battery of tests is to be performed by strictly standardized methods.

1. Red cell, white cell, platelet counts, white blood cell differential, hematacrit and red cell indices must be performed by an accredited laboratory. The normal ranges for the red cell and white cell counts

are influenced by altitude, race, and sex, and therefore should be determined by the accredited laboratory in the specific area where the tests are performed.

Either a decline from an absolute normal or an individual's base line to a subnormal value or a rise to a supra-normal value, are indicative of potential toxicity, particularly if all blood parameters decline. The normal total white blood count is approximately 7,200/mm<sup>3</sup> plus or minus 3,000. For cigarette smokers the white count may be higher and the upper range may be 2,000 cells higher than normal for the laboratory. In addition, infection, allergies and some drugs may raise the white cell count. The normal platelet count is approximately 250,000 with a range of 140,000 to 400,000. Counts outside this range should be regarded as possible evidence of benzene toxicity.

Certain abnormalities found through routine screening are of greater significance in the benzene-exposed worker and require prompt consultation with a specialist, namely:

a. Thrombocytopenia.

b. A trend of decreasing white cell, red cell, or platelet indices in an individual over time is more worrisome than an isolated abnormal finding at one test time. The importance of trend highlights the need to compare an individual's test results to baseline and/or previous periodic tests.

c. A constellation or pattern of abnormalities in the different blood indices is of more significance than a single abnormality. A low white count not associated with any abnormalities in other cell indices may be a normal statistical variation, whereas if the low white count is accompanied by decreases in the platelet and/or red cell indices, such a pattern is more likely to be associated with benzene toxicity and merits thorough investigation.

Anemia, leukopenia, macrocytosis or an abnormal differential white blood cell count should alert the physician to further investigate and/or refer the patient if repeat tests confirm the abnormalities. If routine screening detects an abnormality, follow-up tests which may be helpful in establishing the etiology of the abnormality are the peripheral blood smear and the reticulocyte count.

The extreme range of normal for reticulocytes is 0.4 to 2.5 percent of the red cells, the usual range being 0.5 to 1.2 percent of the red cells, but the typical value is in the range of 0.8 to 1.0 percent. A decline in reticulocytes to levels of less than 0.4 percent is to be regarded as possible evidence (unless another specific cause is found) of benzene toxicity requiring accelerated surveillance. An increase in reticulocyte

levels to about 2.5 percent may also be consistent with (but is not as characteristic of) benzene toxicity.

2. An important diagnostic test is a careful examination of the peripheral blood smear. As with reticulocyte count the smear should be with fresh uncoagulated blood obtained from a needle tip following venipuncture or from a drop of earlobe blood (capillary blood). If necessary, the smear may, under certain limited conditions, be made from a blood sample anticoagulated with EDTA (but never with oxalate or heparin). When the smear is to be prepared from a specimen of venous blood which has been collected by a commercial Vacutainer type tube containing neutral EDTA, the smear should be made as soon as possible after the venesection. A delay of up to 12 hours is permissible between the drawing of the blood specimen into EDTA and the preparation of the smear if the blood is stored at refrigerator (not freezing) temperature.

3. The minimum mandatory observations to be made from the smear are:

- a. The differential white blood cell count.
- b. Description of abnormalities in the appearance of red cells.
- c. Description of any abnormalities in the platelets.
- d. A careful search must be made throughout of every blood smear for immature white cells such as band forms (in more than normal proportion, i.e., over 10 percent of the total differential count), any number of metamyelocytes, myelocytes or myeloblasts. Any nucleate or multinucleated red blood cells should be reported. Large "giant" platelets or fragments of megakaryocytes must be recognized.

An increase in the proportion of band forms among the neutrophilic granulocytes is an abnormality deserving special mention, for it may represent a change which should be considered as an early warning of benzene toxicity in the absence of other causative factors (most commonly infection). Likewise, the appearance of metamyelocytes, in the absence of another probable cause, is to be considered a possible indication of benzene-induced toxicity.

An upward trend in the number of basophils, which normally do not exceed about 2.0 percent of the total white cells, is to be regarded as possible evidence of benzene toxicity. A rise in the eosinophil count is less specific but also may be suspicious of toxicity if the rises above 6.0 percent of the total white count. The normal range of monocytes is from 2.0 to 8.0 percent of the total white count with an average of about 5.0 percent. About 20 percent of individuals

reported to have mild but persisting abnormalities caused by exposure to benzene show a persistent monocytosis. The findings of a monocyte count which persists at more than 10 to 12 percent of the normal white cell count (when the total count is normal) or persistence of an absolute monocyte count in excess of 800/mm<sup>3</sup> should be regarded as a possible sign of benzene-induced toxicity.

A less frequent but more serious indication of benzene toxicity is the finding in the peripheral blood of the so-called "pseudo" (or acquired) Pelger-Huet anomaly. In this anomaly many, or sometimes the majority, of the neutrophilic granulocytes possess two round nuclear segments - less often one or three round segments - rather than three normally elongated segments. When this anomaly is not hereditary, it is often but not invariably predictive of subsequent leukemia. However, only about two percent of patients who ultimately develop acute myelogenous leukemia show the acquired Pelger-Huet anomaly. Other tests that can be administered to investigate blood abnormalities are discussed below; however, such procedures should be undertaken by the hematologist.

An uncommon sign, which cannot be detected from the smear, but can be elicited by a "sucrose water test" of peripheral blood, is transient paroxysmal nocturnal hemoglobinuria (PNH), which may first occur insidiously during a period of established aplastic anemia, and may be followed within one to a few years by the appearance of rapidly fatal acute myelogenous leukemia. Clinical detection of PNH, which occurs in only one or two percent of those destined to have acute myelogenous leukemia, may be difficult; if the "sucrose water test" is positive, the somewhat more definitive Ham test, also known as the acid-serum hemolysis test, may provide confirmation.

e. Individuals documented to have developed acute myelogenous leukemia years after initial exposure to benzene may have progressed through a preliminary phase of hematologic abnormality. In some instances pancytopenia (i.e., a lowering in the counts of all circulating blood cells of bone marrow origin, but not to the extent implied by the term "aplastic anemia") preceded leukemia for many years. Depression of a single blood cell type or platelets may represent a harbinger of aplasia or leukemia. The finding of two or more cytopenias, or pancytopenia in a benzene-exposed individual, must be regarded as highly suspicious of more advanced although still reversible, toxicity. "Pancytopenia" coupled with the appearance of immature cells (myelocytes, myeloblasts, erythroblasts, etc.), with abnormal cells (pseudo Pelger-Huet anomaly, atypical nuclear heterochromatin, etc.), or unexplained elevations of white blood cells must be regarded as evidence of benzene overexposure.

unless proved otherwise. Many severely aplastic patients manifested the ominous finding of 5-10 percent myeloblasts in the marrow, occasional myeloblasts and myelocytes in the blood and 20-30% monocytes. It is evident that isolated cytopenias, pancytopenias, and even aplastic anemias induced by benzene may be reversible and complete recovery has been reported on cessation of exposure. However, since any of these abnormalities is serious, the employee must immediately be removed from any possible exposure to benzene vapor. Certain tests may substantiate the employee's prospects for progression or regression. One such test would be an examination of the bone marrow, but the decision to perform a bone marrow aspiration or needle biopsy is made by the hematologist.

The findings of basophilic stippling in circulating red blood cells (usually found in 1 to 5% of red cells following marrow injury), and detection in the bone marrow of what are termed "ringed sideroblasts" must be taken seriously, as they have been noted in recent years to be premonitory signs of subsequent leukemia.

Recently peroxidase-staining of circulating or marrow neutrophil granulocytes, employing benzidine dihydrochloride, have revealed the disappearance of, or diminution in, peroxidase in a sizable proportion of the granulocytes, and this has been reported as an early sign of leukemia. However, relatively few patients have been studied to date. Granulocyte granules are normally strongly peroxidase positive. A steady decline in leukocyte alkaline phosphatase has also been reported as suggestive of early acute leukemia. Exposure to benzene may cause an early rise in serum iron, often but not always associated with a fall in the reticulocyte count. Thus, serial measurements of serum iron levels may provide a means of determining whether or not there is a trend representing sustained suppression of erythropoiesis.

Measurement of serum iron, determination of peroxidase and of alkaline phosphatase activity in peripheral granulocytes can be performed in most pathology laboratories. Peroxidase and alkaline phosphatase staining are usually undertaken when the index of suspicion for leukemia is high.

#### **APPENDIX D**

##### **SAMPLING AND ANALYTICAL METHODS FOR BENZENE MONITORING AND MEASUREMENT**

Measurements taken for the purpose of determining employee exposure to benzene are best taken so that the representative average 8-hour exposure may be determined from a single 8-hour sample or two (2) 4-hour samples. Short-time interval samples

(or grab samples) may also be used to determine average exposure level if a minimum of five measurements are taken in a random manner over the 8-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random samples taken on one work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling and analysis must be performed with procedures meeting the requirements of the standard.

There are a number of methods available for monitoring employee exposures to benzene. The sampling and analysis may be performed by collection of the benzene vapor or charcoal absorption tubes, with subsequent chemical analysis by gas chromatography. Sampling and analysis may also be performed by portable direct reading instruments, real-time continuous monitoring systems, passive dosimeters or other suitable methods. The employer has the obligation of selecting a monitoring method which meets the accuracy and precision requirements of the standard under his unique field conditions. The standard requires that the method of monitoring must have an accuracy, to a 95 percent confidence level, of not less than plus or minus 25 percent for concentrations of benzene greater than or equal to 0.5 ppm.

The OSHA Laboratory modified NIOSH Method S311 and evaluated it at a benzene air concentration of 1 ppm. A procedure for determining the benzene concentration in bulk material samples was also evaluated. This work, reported in OSHA Laboratory Method No. 12, includes the following two analytical procedures:

#### **I. OSHA Method 12 for Air Samples**

Analyte: Benzene Matrix: Air Procedure: Adsorption on charcoal, desorption with carbon disulfide, analysis by GC. Detection limit: 0.04 ppm Recommended air volume and sampling rate: 10L to 0.2 L/min.

##### **1. Principle of the Method.**

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2. The charcoal in the tube is transferred to a small, stoppered vial, and the analyte is desorbed with carbon disulfide.

1.3. An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from standards.

## 2. Advantages and disadvantages of the method.

2.1 The sampling device is small, portable, and involved no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The samples are analyzed by means of a quick, instrumental method.

2.2 The amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25 percent of that found on the front section, the possibility of sample loss exists.

## 3. Apparatus.

3.1 A calibrated personal sampling pump whose flow can be determined within (+ or -) 5 percent at the recommended flow rate.

3.2. Charcoal tubes: Glass with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 deg. C prior to packing. The adsorbing section contains 100 mg of charcoal, the back-up section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the back-up section. A plug of silanized glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

3.3. Gas chromatograph equipped with a flame ionization detector.

3.4. Column (10-ft X 1/8 -in stainless steel) packed with 80/100 Supelcoport coated with 20 percent SP 2100, 0.1 percent CW 1500.

3.5. An electronic integrator or some other suitable method for measuring peak area.

3.6. Two-milliliter sample vials with Teflon-lined caps.

3.7. Microliter syringes: 10-microliter (10-uL syringe, and other convenient sizes for making standards, 1-uL syringe for sample injections.

3.8. Pipets: 1.0 mL delivery pipets

3.9. Volumetric flasks: convenient sizes for making standard solutions.

## 4. Reagents.

4.1. Chromatographic quality carbon disulfide (CS(2)). Most commercially available carbon disulfide contains a trace of benzene which must be removed. It can be removed with the following procedure:

Heat under reflux for 2 to 3 hours, 500 mL of carbon disulfide, 10 mL concentrated sulfuric acid, and 5 drops of concentrated nitric acid. The benzene is converted to nitrobenzene. The carbon disulfide layer is removed, dried with anhydrous sodium sulfate, and distilled. The recovered carbon disulfide should be benzene free. (It has recently been determined that benzene can also be removed by passing the carbon disulfide through 13x molecular sieve).

4.2. Benzene, reagent grade.

4.3. p-Cymene, reagent grade, (internal standard).

4.4. Desorbing reagent. The desorbing reagent is prepared by adding 0.05 mL of p-cymene per milliliter of carbon disulfide. (The internal standard offers a convenient means correcting analytical response for slight inconsistencies in the size of sample injections. If the external standard technique is preferred, the internal standard can be eliminated).

4.5. Purified GC grade helium, hydrogen and air.

## 5. Procedure.

5.1. Cleaning of equipment. All glassware used for the laboratory analysis should be properly cleaned and free of organics which could interfere in the analysis.

5.2. Calibration of personal pumps. Each pump must be calibrated with a representative charcoal tube in the line.

5.3. Collection and shipping of samples.

5.3.1. Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

5.3.2. The smaller section of the charcoal is used as the backup and should be placed nearest the sampling pump.

5.3.3. The charcoal tube should be placed in a vertical position during sampling to minimize channeling through the charcoal.

5.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

5.3.5. A sample size of 10 liters is recommended. Sample at a flow rate of approximately 0.2 liters per minute. The flow rate should be known with an accuracy of at least (+ or -) 5 percent.

5.3.6. The charcoal tubes should be capped with the supplied plastic caps immediately after sampling.

5.3.7. Submit at least one blank tube (a charcoal tube subjected to the same handling procedures, without having any air drawn through it) with each set of samples.

5.3.8. Take necessary shipping and packing precautions to minimize breakage of samples.

#### 5.4. Analysis of samples.

5.4.1. Preparation of samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml vial. The separating section of foam is removed and discarded; the second section is transferred to another capped vial. These two sections are analyzed separately.

5.4.2. Desorption of samples. Prior to analysis, 1.0 mL of desorbing solution is pipetted into each sample container. The desorbing solution consists of 0.05  $\mu$ L internal standard per mL of carbon disulfide. The sample vials are capped as soon as the solvent is added. Desorption should be done for 30 minutes with occasional shaking.

5.4.3. GC conditions. Typical operating conditions for the gas chromatograph are:

1.30 mL/min (60 psig) helium carrier gas flow.

2.30 mL/min (40 psig) hydrogen gas flow to detector.

3.240 mL/min (40 psig) air flow to detector.

4.150 deg. C injector temperature.

5.250 deg. C detector temperature.

6.100 deg. C column temperature.

5.4.4. Injection size. 1  $\mu$ L.

5.4.5. Measurement of area. The peak areas are measured by an electronic integrator or some other suitable form of area measurement.

5.4.6. An internal standard procedure is used. The integrator is calibrated to report results in ppm for a 10 liter air sample after correction for desorption efficiency.

#### 5.5. Determination of desorption efficiency.

5.5.1. Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and from one lot of chemical to another. Thus, it is necessary to determine, at least once, the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

5.5.2. Procedure for determining desorption efficiency. The reference portion of the charcoal tube is removed. To the remaining portion, amounts representing 0.5X, 1X, and 2X and (X represents target concentration) based on a 10 L air sample are injected into several tubes at each level. Dilutions of benzene with carbon disulfide are made to allow injection of measurable quantities. These tubes are then allowed to equilibrate at least overnight. Following equilibration they are analyzed following the same procedure as the samples. Desorption efficiency is determined by dividing the amount of benzene found by amount spiked on the tube.

**6. Calibration and standards.** A series of standards varying in concentration over the range of interest is prepared and analyzed under the same GC conditions that will be used on the samples. A calibration curve is prepared by plotting concentration ( $\mu$ g/mL) versus peak area.

**7. Calculations.** Benzene air concentration can be calculated from the following equation:

$$\text{mg/m}^3 = (A)(B)/(C)(D)$$

Where: A =  $\mu$ g/mL benzene, obtained from the calibration curve

B = desorption volume (1 mL)

C = Liters of air sampled

D = desorption efficiency

The concentration in mg/m<sup>3</sup> can be converted to ppm (at 25 deg. and 760 mm) with following equation:

$$\text{ppm} = (\text{mg/m}^3)(24.46)/(78.11)$$

Where: 24.46 = molar volume of an ideal gas 25 deg. C and 760 mm

78.11 = molecular weight of benzene



## 8. Backup Data.

### 8.1 Detection limit-Air Samples.

The detection limit for the analytical procedure is 1.28 ng with a coefficient of variation of 0.023 at this level. This would be equivalent to an air concentration of 0.04 ppm for a 10 L air sample. This amount provided a chromatographic peak that could be identifiable in the presence of possible interferences. The detection limit data were obtained by making 1 uL injections of a 1.283 ug/mL standard.

INJECTION	AREA COUNT	
1	655.4	
2	617.5	
3	662.0	X = 640.2
4	641.1	SD = 14.9
5	636.4	CV = 0.023
6	629.2	

### 8.2. Pooled coefficient of variation - Air Samples.

The pooled coefficient of variation for the analytical procedure was determined by 1 uL replicate injections of analytical standards. The standards were 16.04, 32.08, and 64.16 ug/mL, which are equivalent to 0.5, 1.0, and 2.0 ppm for a 10 L air sample respectively.

INJECTION	AREA COUNTS		
	0.5 ppm	1.0 ppm	2.0 ppm
1	3996.5	8130.2	16481
2	4059.4	8235.6	16493
3	4052.0	8307.9	16535
4	4027.2	8263.2	16609
5	4046.8	8291.1	16552
6	4137.9	8288.8	16618
X=	4053.3	8254.0	16548.3
SD=	47.2	62.5	57.1
CV=	0.0116	0.0076	0.0034
CV=0.008			

### 8.3. Storage data - Air Samples

Samples were generated at 1.03 ppm benzene at 80% relative humidity, 22 deg. C, and 643 mm. All samples were taken for 50 minutes at 0.2 L/min. Six samples were analyzed immediately and the rest of the samples were divided into two groups by fifteen samples each. One group was stored at refrigerated temperature of 25 deg. C, and the other group was stored at ambient temperature (approximately 23 deg. C). These samples were analyzed over a period of fifteen days. The results are tabulated below.

#### PERCENT RECOVERY

Day analyzed	Refrigerated			Ambient		
0	97.4	98.7	98.9	97.4	98.7	98.9
0	97.1	100.6	100.9	97.1	100.6	100.9
2	95.8	96.4	95.4	95.4	96.6	96.9
5	93.9	93.7	92.4	92.4	94.3	94.1
9	93.6	95.5	94.6	95.2	95.6	96.6
13	94.3	95.3	93.7	91.0	95.0	94.6
15	96.8	95.8	94.2	92.9	96.3	95.9

### 8.4. Desorption data.

Samples were prepared by injecting liquid benzene onto the A section of charcoal tubes. Samples were prepared that would be equivalent to 0.5, 1.0, and 2.0 ppm for a 10 L air sample.

#### PERCENT RECOVERY

Sample	0.5 ppm	1.0 ppm	2.0 ppm
1	99.4	98.8	99.5
2	99.5	98.7	99.7
3	99.2	98.6	99.8
4	99.4	99.1	100.0
5	99.2	99.0	99.7
6	99.8	99.1	99.9
X=	99.4	98.9	99.8
SD=	0.22	0.21	0.18
CV=	0.0022	0.0021	0.0018
X = 99.4			

### 8.5. Carbon disulfide.

Carbon disulfide from a number of sources was analyzed for benzene contamination. The results are given in the following table. The benzene contaminant can be removed with the procedures given in section 4.1.

Sample	ug Benzene/ mL	ppm equivalent (for 10 L air sample)
Aldrich Lot 83017	4.20	0.13
Baker Lot 720364	1.01	0.03
Baker Lot 822351	1.01	0.03
Malinkrodt Lot WEMP	1.74	0.05
Malinkrodt Lot WDSJ	5.65	0.18
Malinkrodt Lot WHGA	2.90	0.09
Treated CS <sub>2</sub>		

## II. OSHA LABORATORY METHOD NO. 12 FOR BULK SAMPLES

Analyte: Benzene.

Matrix: Bulk Samples.

Procedure: Bulk Samples are analyzed directly by high performance liquid chromatography (HPLC).

Detection limits: 0.01% by volume.

### 1. Principle of the method.

1.1. An aliquot of the bulk sample to be analyzed is injected into a liquid chromatograph.

1.2. The peak area for benzene is determined and compared to areas obtained from standards.

### 2. Advantages and disadvantages of the method.

2.1. The analytical procedure is quick, sensitive, and reproducible.

2.2. Reanalysis of samples is possible.

2.3. Interferences can be circumvented by proper selection of HPLC parameters.

2.4. Samples must be free of any particulates that may clog the capillary tubing in the liquid chromatograph. This may require distilling the sample or clarifying with a clarification kit.

### 3. Apparatus.

3.1. Liquid chromatograph equipped with a UV detector.

3.2. HPLC Column that will separate benzene from other components in the bulk sample being analyzed. The column used for validation studies was a Waters uBondapack C18, 30 cm x 3.9 mm.

3.3. A clarification kit to remove any particulates in the bulk if necessary.

3.4. A micro-distillation apparatus to distill any samples if necessary.

3.5. An electronic integrator or some other suitable method of measuring peak areas.

3.6. Microliter syringes - 10 uL syringe and other convenient sizes for making standards. 10 uL syringe for sample injections.

3.7. Volumetric flasks, 5 mL and other convenient sizes for preparing standards and making dilutions.

### 4. Reagents.

4.1. Benzene, reagent grade.

4.2. HPLC grade water, methyl alcohol, and isopropyl alcohol.

### 5. Collection and shipment of samples.

5.1. Samples should be transported in glass containers with Teflon-lined caps.

5.2. Samples should not be put in the same container used for air samples.

### 6. Analysis of samples.

6.1. Sample preparation.

If necessary, the samples are distilled or clarified. Samples are analyzed undiluted. If the benzene concentration is out of the working range, suitable dilutions are made with isopropyl alcohol.

6.2. HPLC conditions.

The typical operating conditions for the high performance liquid chromatograph are:

1. Mobile phase - Methyl alcohol/water, 50/50

1. Analytical wavelength - 254 nm

3. Injection size - 10 uL

### 6.3. Measurement of peak area and calibration.

Peak areas are measured by an integrator or other suitable means. The integrator is calibrated to report results % in benzene by volume.

## 7. Calculations.

Since the integrator is programmed to report results in % benzene by volume in an undiluted sample, the following equation is used:

$$\% \text{ Benzene by Volume} = A \times B$$

Where: A = % by volume on report

B = Dilution Factor

(B = 1 for undiluted sample)

## 8. Backup Data.

### 8.1. Detection limit - Bulk Samples.

The detection limit for the analytical procedure for bulk samples is 0.88 ug, with a coefficient of

variation of 0.019 at this level. This amount provided a chromatographic peak that could be identifiable in the presence of possible interferences. The detection limit data were obtained by making 10 uL injections of a 0.10% by volume standard.

Injection	Area Count	
1	45386	
2	44214	
3	43822	X = 44040.1
4	44062	SD = 852.5
6	42724	CV = 0.019

### 8.2. Pooled coefficient of variation - Bulk Samples.

The pooled coefficient of variation for analytical procedure was determined by 50 uL replicate injections of analytical standards. The standards were 0.01, 0.02, 0.04, 0.10, 1.0, and 2.0% benzene by volume.

#### AREA COUNT (PERCENT)

Injection No.	0.01	0.02	0.04	0.10	1.0	2.0
1	45386	84737	166097	448497	4395380	9339150
2	44241	84300	170832	441299	4590800	9484900
3	43822	83835	164160	443719	4593200	9557580
4	44062	84381	164445	444842	4642350	9677060
5	44006	83012	168398	442564	4646430	9766240
6	42724	81957	173002	443975	4646260	
X =	44040.1	83703.6	167872	444149	4585767	9564986
SD =	852.5	1042.2	3589.8	2459.1	96839.3	166233
CV =	0.0194	0.0125	0.0213	0.0055	0.0211	0.0174
CV =	0.017					